

Potential Chlorpyrifos Exposure to Residents Following Standard Crack and Crevice Treatment

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Multipathway exposures were evaluated for residents of houses over a 10-day period following a crack and crevice application of a chlorpyrifos-based formulation. Three multiroom houses with two adults each were treated. Air concentration, total deposition, and dislodgeable residues on horizontal surfaces were measured to assess potential respiratory, oral, and dermal exposures, respectively, in treated and untreated high activity rooms. In addition, urine samples collected from the adults were analyzed for the primary metabolite of chlorpyrifos, 3,5,6-trichloropyridinol, to determine absorbed dose. The maximum chlorpyrifos air concentration observed was 2.3 $\mu\text{g}/\text{m}^3$, with air concentrations generally decreasing to levels ranging from 0.1 to 0.3 $\mu\text{g}/\text{m}^3$ within 10 days. Carpet dislodgeable residues, used to evaluate the amount of residues potentially transferred upon contact, were less than the analytical method limit of quantitation (1.6 $\mu\text{g}/\text{m}^2$). Hard plastic balls placed in the homes on the day before application contained no detectable dislodgeable residues (<6.5 $\mu\text{g}/\text{m}^2$). Ten-day cumulative nontarget residues deposited on surfaces, as determined by deposition pads, were less than 2.3 $\mu\text{g}/100\text{ cm}^2$. Deposition samples from all living area floors collected 2 hr after application contained less than 9.9 $\mu\text{g}/100\text{ cm}^2$. Therefore, contact with household surfaces and subsequent hand-to-mouth activity are not expected to significantly contribute to overall exposure. Estimated exposures to children, based on the passive dosimetry measurements, ranged from 0.26 to 2.1% of the no observed effect level for plasma cholinesterase depression. In addition, potential exposures to the adult residents, as indicated by the urinary 3,5,6-TCP biomonitoring, did not increase as a result of the application. *Key words:* children's toys, chlorpyrifos, dislodgeable residues, nondietary exposure and dose, particle deposition, pesticide application, pesticide residuals, semivolatile pesticide, surface wipes, urinary biomonitoring. *Environ Health Perspect* 106:725–731 (1998). [Online 14 October 1998] <http://ehpnet1.niehs.nih.gov/docs/1998/106p725-731byrne/abstract.html>

Chlorpyrifos is used for structural, crack and crevice, and outdoor turf and perimeter treatments for the control of pests in the urban environment. Because of widespread urban and agricultural uses, numerous toxicity and exposure studies have been conducted over the past 30 years to ensure that chlorpyrifos-containing products are safe for both applicators and residents of the treated homes. However, few studies have evaluated potential multipathway exposures to adults and children following a crack and crevice treatment—the primary indoor use pattern for chlorpyrifos products. Moreover, few studies have been conducted in occupied multiroom homes.

Previously, studies have been performed to assess exposures to occupants following broadcast and fogging treatments using chlorpyrifos (1–4). When treated by these methods, a large volume of a chlorpyrifos-containing solution is applied to continuous floor areas. In contrast, a crack and crevice application consists of a directed pinpoint stream to baseboards and other cracks harboring pests. Therefore, because residents are less prone to contact these relatively inaccessible surfaces directly, potential occupant exposure should be lower following a crack and crevice treatment than either a broadcast or fogger treatment.

Three studies by Wright et al. (5–7) provide limited data on indoor environmental levels of chlorpyrifos following crack and crevice treatments. In 1978, Wright and Leidy (5) measured chlorpyrifos concentrations in vacant rooms following the application of a 0.5% or 1% solution with either an aerosol-type or compressed-air sprayer. Air samples were collected in each of four rooms immediately following application and at 1-, 2-, and 3-day intervals after application. For all dilutions and treatments, chlorpyrifos concentrations ranged from 0.6 to 2.7 $\mu\text{g}/\text{m}^3$ immediately following application and decreased to 0.07–0.2 $\mu\text{g}/\text{m}^3$ at 3 days after application. These data demonstrated that air concentrations immediately following application were low relative to the proposed National Academy of Sciences (NAS) 24-hr continuous exposure guideline (10 $\mu\text{g}/\text{m}^3$) and declined over the 3-day follow-up period.

In 1975, Wright and Jackson (6) studied residual chlorpyrifos levels on nontreated surfaces for up to 8 days following a crack and crevice treatment. In this study, four vacant dormitory rooms were treated with a 0.5% or 1.0% solution of chlorpyrifos. Floor deposition values for chlorpyrifos ranged from 4 to 35 $\mu\text{g}/\text{m}^2$ for the

0.5% dilution and from 4 to 113 $\mu\text{g}/\text{m}^2$ for the 1% dilution. These values represented approximately 0.1% of the calculated deposition levels expected from a uniform broadcast application using a 0.5% solution. Therefore, potential dermal exposures should be negligible following a crack and crevice application.

This study was designed to measure potential multipathway exposures to residents living in multiroom homes treated with chlorpyrifos. Dosimetry techniques consisting of air, total surface, and dislodgeable residues from carpet and surrogate toy dosimeters were collected to evaluate potential exposures to children living in the home. In addition, urinary biomonitoring was conducted for adults to directly estimate total chlorpyrifos absorbed postapplication.

Methods

Application of test material. To evaluate exposure in actual homes, three occupied single-family homes near Indianapolis, Indiana, were selected for this study. The houses varied in size (90–150 m^2) and style. Except for the addition of sampling equipment, no attempt was made to change the furnishings of the home.

The Dursban Pro insecticide (Dow AgroSciences LLC, Indianapolis, IN), as a 0.5% water emulsion, was prepared according to current EPA-accepted label instructions. The amount of Dursban Pro solution applied to each house ranged from 663 ml to 787 ml, containing 3.32 g–3.94 g chlorpyrifos, respectively.

The crack and crevice treatment, with limited spot treatments, is a typical treatment for a German cockroach infestation. A licensed applicator treated all three structures in a similar manner using a gallon-size B & G sprayer (B & G Equipment Co., Plumsteadville, PA) equipped with a pressure regulator and an adaptable spray-nozzle tip, according to standard procedures for cockroach control. In the treated rooms (kitchen, bathrooms, and other areas potentially harboring cockroaches), all materials were removed prior to application; this included emptying all cabinets, drawers, and

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Received 24 March 1998; accepted 29 June 1998.

the pantry pursuant to standard practices. A crack and crevice injector tip was used to apply the test material to where two surfaces meet inside cabinets, pantry, vanity, and drawers (e.g., side and back, back and top, side and bottom, etc.); to the crack between the baseboard and wall; along the counter-top backsplash-wall interface; under eating table(s); and around the toilet base. The fine fan tip was used to apply test material in a band approximately one-third meter wide under sinks, to the underside of shelves and tables, under large appliances such as a refrigerator, and to the underside of drawers (while drawers were removed). The pin stream tip was used only intermittently to spray behind large appliances such as a washing machine. Mechanical ventilation and air flow in each house was limited to maximize potential exposure to chlorpyrifos. In general, the windows remained closed, and the air conditioning and heating remained off.

Human volunteers. Urine samples were only collected from adults. Children were specifically excluded from this study due to logistical concerns related to the continuous collection of cumulative urine samples (see Biomonitoring). The six volunteers ranged in age from 29 to 62 years and consisted of four women and two men. The volunteers, two per home, were asked to follow their normal routines during the course of this study. The volunteers were instructed to remain outside of any treated room during treatment pursuant to standard label recommendations, but were not otherwise restricted. The volunteers were instructed to spend at least 12 hr/day inside the treated home, which was verified by a log maintained by each volunteer.

Air monitoring. Continuous air sampling for chlorpyrifos vapor and aerosol was conducted for 10 days postapplication. Samples were collected from the kitchen (treated area) and another untreated adjacent room, such as a family room, where residents spent a large portion of their time. At each sampling location, separate air samples were collected at approximately 0.4 m and 1.3 m above the floor, representing the potential breathing zones of a crawling child and standing adult, respectively. Air samples were drawn through a mixed cellulose ester filter followed by Chromosorb 102 (SKC Inc., Eighty Four, PA) back-up tube by a continuously operated, portable battery-operated vacuum pump at a flow rate of 0.7–2.0 l/min. Temperatures in both the family room and bedroom were recorded during each sampling interval and averaged. The filters and Chromosorb tubes were extracted with 5 ml hexane and analyzed by gas chromatography (GC) with an

electron capture detector (ECD). The method had a limit of detection (LOD) of 0.006 $\mu\text{g}/\text{m}^3$ and a limit of quantitation (LOQ) of 0.02 $\mu\text{g}/\text{m}^3$ for both filters and Chromosorb tubes (8). Concurrent laboratory spiked recoveries were greater than 92%, with no observed losses during the storage before analysis.

Deposition pads. To measure total chlorpyrifos deposition onto nontarget horizontal surfaces, 100-cm² denim cloth pads were placed on horizontal surfaces. The denim cloth pads were placed on the floor prior to application in two rooms where children typically spend considerable time, such as a family room and bedroom. The pads were collected at various time intervals after application and analyzed for cumulative chlorpyrifos loading. In addition, 100-cm² denim cloth pads were placed in both treated and nontreated rooms and collected 2 hr following the application. The pads were extracted with 20 ml isooctane, and the extracts were analyzed by GC/ECD. The method LOD was 0.067 $\mu\text{g}/100\text{ cm}^2$ and the LOQ was 0.2 $\mu\text{g}/100\text{ cm}^2$ (8). Average laboratory recoveries for all cloth samples, including the two described below, were 110.0–115.2%.

Dislodgeable residues (hard-toy wipes and carpet drags). Passive dosimetry techniques were used to measure dislodgeable, or bioavailable, chlorpyrifos residues on horizontal surfaces. Small plastic toy balls (8-cm diameter; Toys “R” Us, Paramus, NJ) were employed as surrogate dosimeters to determine the potential dislodgeability of residues from domestic surfaces. In addition, a weighted drag sled was used to evaluate potential dermal exposures to individuals when crawling upon carpeted surfaces within the home.

Sixteen 8-cm diameter plastic toy balls were placed on the carpet prior to application adjacent to the deposition pads. A single ball was randomly selected for sampling at a predetermined interval. To ensure complete contact with the carpeted surface, the ball was “putted” 10 times across the entire length of the room. The ball was then thoroughly wiped with two 100-cm² denim cloth squares to estimate potential dislodgeable residues. The cloth squares were analyzed as described above for the deposition pads, except 40-ml isooctane was used to extract both cloth squares simultaneously.

Carpet drag samples were also collected adjacent to the deposition pads for up to 10 days after treatment using the weighted drag sled; this sled was designed to exert the approximate pressure of a 10-kg child standing and/or crawling across the carpeted surface (9). A 100-cm² piece of denim cloth

was affixed to the bottom of the sled and pulled across 1.2 m of carpeted floor, simulating a sheering motion similar to crawling. Each “lane” (0.12 m²) was sampled only once. Upon completion of the drag, the denim cloth was removed and analyzed as described above for the deposition pads.

Biomonitoring. The adult volunteers collected all urine voided on the day before application (day -1), the day of application (initial exposure), and for 10 consecutive days following the initial exposure. The urine was analyzed for 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) (10) by acid hydrolyzing 1.0 ml of urine spiked with 10 μl of a ¹³C₂ ¹⁵N-3,5,6-TCP internal standard solution, which was then extracted with 1.0 ml 1-chlorobutane and derivatized with *N*-methyl-*N*-[*tert*-butyldimethylsilyl]trifluoroacetamide to form the *tert*-butyldimethylsilyl derivative. The derivative was quantified by gas chromatography with mass selective detection (GC/MSD). The method had an LOD of 0.31 ng/ml and an LOQ of 2 ng/ml (11). Recoveries of 3,5,6-TCP from 3,5,6-TCP-spiked urine of unexposed individuals, from 3,5,6-TCP spiked into the volunteers preexposure urine, and from 3,5,6-TCP fortified concurrent laboratory samples ranged from 85 to 123%. The 3,5,6-TCP in urine was stable during the brief storage period before analysis.

Urinary creatinine was quantified using Sigma Diagnostics Creatinine Analysis Kit #555-A (Sigma, St. Louis, MO) by measuring the initial and final absorbance of the samples at 500 nm. Urine collections were considered to be complete if the average creatinine excretion rate was within or exceeded the literature range for creatinine excretion (12) and/or the creatinine excretion rate was consistent with the other urine samples provided by that volunteer. Based on these criteria, the amount of 3,5,6-TCP measured in the urine was adjusted for the amount of creatinine produced in a given 24-hr period, if necessary. Based upon the consistency between the amount of creatinine measured in each sample and standard excretion rates for adults, each urine sample was deemed to be complete.

Results

Analysis of air samples. The air monitoring results are summarized in Figure 1. Air concentrations measured in the treated kitchen and at the 1.3-m height were generally higher than those measured in the adjacent family room and at the 0.4-m height. In house #1, the airborne chlorpyrifos levels peaked at 0.76 $\mu\text{g}/\text{m}^3$, at 0–2 hr after application at 1.3 m above the kitchen floor. Peak concentrations of 2.3 $\mu\text{g}/\text{m}^3$ and 1.7 $\mu\text{g}/\text{m}^3$ were measured at 60–72 hr and

at 6–8 hr in houses #2 and #3, respectively, at the 0.4-m sampling height. Low chlorpyrifos concentrations were measured in house #3 before application. This was probably due to a previous chlorpyrifos dust application noted by the residents.

Airborne concentrations decreased to pretreatment levels by 7 days after application in all the homes. In houses #1 and #3, air concentrations generally declined after approximately 8 hr. However, peak air concentrations were observed on the third and sixth days in house #2. These peak concentrations seemed to correlate well with the fluctuation of internal temperatures.

Measured air concentrations and daily means are summarized in Table 1. All air concentrations were at least fourfold less than the proposed NAS 24-hr continuous exposure guideline of $10 \mu\text{g}/\text{m}^3$. Air concentrations measured at the 1.3-m height were usually slightly higher than those measured at the 0.4-m height in all monitored rooms, with the exception of the samples collected in the kitchen in house #2. Compared to measurements reported by Fenske et al. (13) in which air concentrations above a treated carpet were greater closer to the floor, air concentrations following a crack and crevice treatment did not exhibit such a pattern. Because chlorpyrifos is not applied directly to floors during a crack and crevice application, it is not surprising that a concentration gradient attributed to volatilization was not observed above the floor (see Application of Test Material).

Deposition pads. The results from the 10-day cumulative deposition pads can be found in Table 2. These results represented the cumulative loading of total chlorpyrifos residues over time on surfaces such as soft toys or upholstered furniture in high activity rooms adjacent to treated rooms. As with any indoor chemical use, some non-target deposition may occur after a crack and crevice application through volatilization, passive transport, and redeposition onto nontreated horizontal surfaces such as carpets, furniture, and soft or plush toys. Thus, a resident of a recently treated home may be potentially exposed to pesticide residues through dermal contact and incidental oral uptake following manual contact with surfaces or objects within the home. Residues of chlorpyrifos on deposition pads from houses #1 and #2 were found at $\leq 0.4 \mu\text{g}/100 \text{ cm}^2$. Peak residues from house #3 were approximately $1.2 \mu\text{g}/100 \text{ cm}^2$ at 6–10 days after application (range: $1.1\text{--}1.3 \mu\text{g}/100 \text{ cm}^2$). Both background and deposition pad residue levels from house #3 were comparatively higher than in the other homes. This may be due to the previous chlorpyrifos application

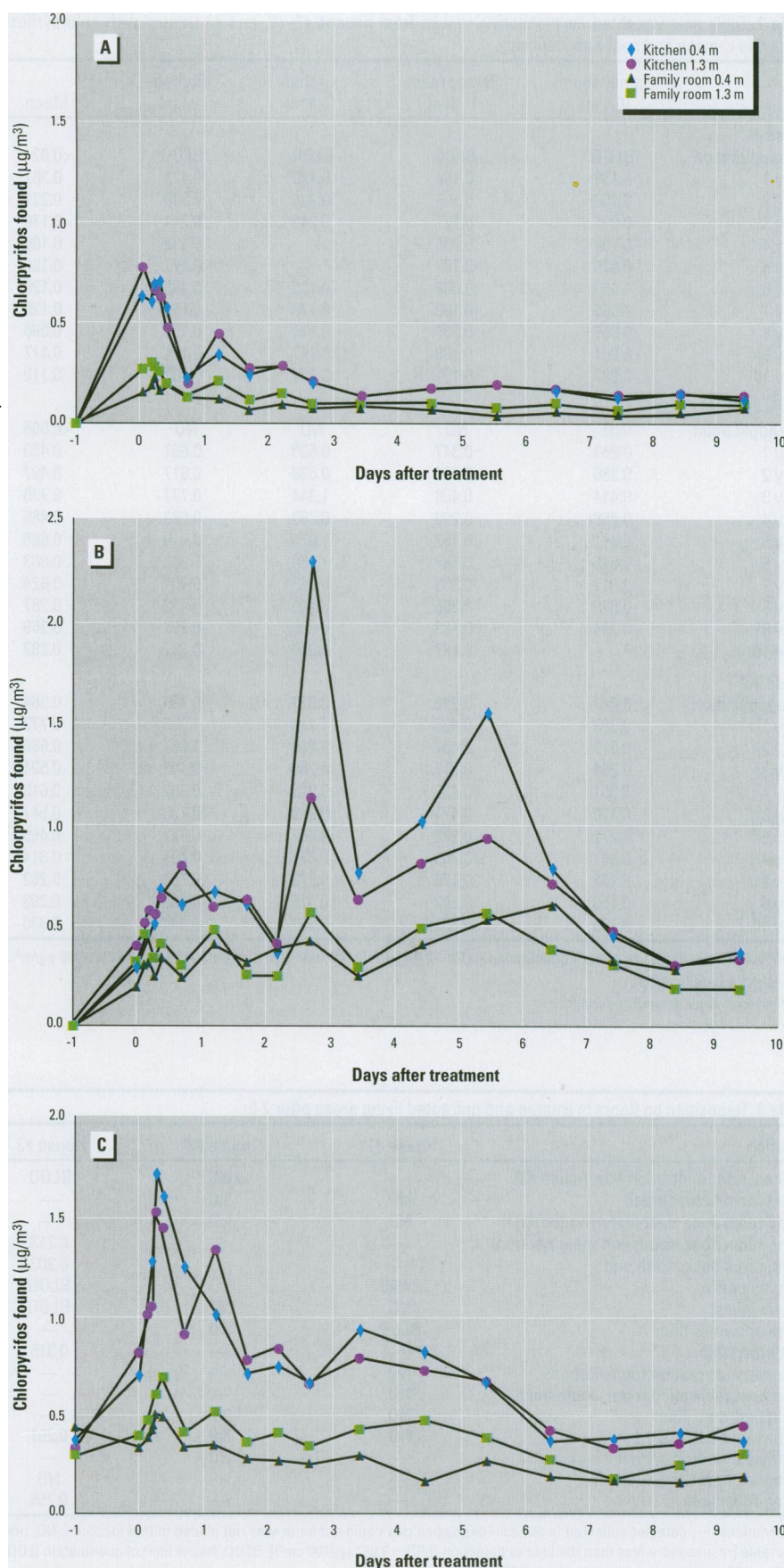


Figure 1. Air concentrations of chlorpyrifos in houses #1 (A), #2 (B), and #3 (C) resulting from residential crack and crevice and spot applications of Dursban Pro.

Table 1. Daily time weighted air monitoring results from houses #1, #2, and #3 treated with chlorpyrifos crack and crevice and spot applications

	Family room (0.4 m)	Family room (1.3 m)	Kitchen (0.4 m)	Kitchen (1.3 m)	Mean
House #1					
Preapplication	BLOQ	BLOQ	BLOQ	BLOQ	<0.02
Day 1	0.159	0.194	0.429	0.423	0.301
Day 2	0.100	0.156	0.280	0.346	0.221
Day 3	0.094	0.127	0.240	0.241	0.176
Day 4	0.100	0.085	^a	0.132	0.106
Day 5	0.075	0.107	^a	0.177	0.120
Day 6	0.050	0.088	0.185	0.188	0.128
Day 7	0.065	0.103	0.170	0.166	0.126
Day 8	0.056	0.067	0.124	0.136	0.096
Day 9	0.061	0.108	0.147	0.151	0.117
Day 10	0.087	0.101	0.124	0.137	0.112
House #2					
Preapplication	ND	ND	ND	ND	<0.006
Day 1	0.263	0.347	0.530	0.661	0.450
Day 2	0.366	0.368	0.638	0.617	0.497
Day 3	0.414	0.408	1.344	0.777	0.736
Day 4	0.258	0.290	0.760	0.633	0.485
Day 5	0.411	0.492	1.025	0.810	0.685
Day 6	0.545	0.567	1.560	0.938	0.903
Day 7	0.617	0.389	0.783	0.708	0.624
Day 8	0.326	0.306	0.445	0.472	0.387
Day 9	0.294	0.183	0.303	0.297	0.269
Day 10	^a	0.187	0.356	0.332	0.292
House #3					
Preapplication	0.442	0.296	0.377	0.339	0.364
Day 1	0.383	0.466	1.218	1.023	0.773
Day 2	0.319	0.437	0.861	1.057	0.669
Day 3	0.264	0.377	0.708	0.746	0.524
Day 4	0.301	0.432	0.928	0.792	0.613
Day 5	0.170	0.474	0.819	0.726	0.547
Day 6	0.271	0.382	0.667	0.672	0.498
Day 7	0.191	0.269	0.371	0.425	0.314
Day 8	0.165	0.176	0.373	0.334	0.262
Day 9	0.156	0.242	0.415	0.358	0.293
Day 10	0.196	0.308	0.367	0.448	0.330

Abbreviations: BLOQ, below limit of quantitation (LOQ = 0.02 µg/m³); ND, not detected (limit of detection = 0.006 µg/m³). Values shown are in µg/m³.

^aNo data reported due to sampling pump failure.

Table 3. Deposition on floors in treated and untreated living areas after 2 hr

Location	House #1	House #2	House #3
Kitchen, floor center (on box, house #3)	—	9.881 ^a	BLOQ
Living room floor, center	ND	ND	—
Living room floor, east (west, house #2)	ND	ND	—
Living room floor, south end (near kitchen)	—	—	0.213
Living room floor, north end	—	—	0.203
Hallway east	0.438 ^b	ND	BLOQ
Hallway west	ND	ND	BLOQ
South entryway floor	BLOQ	ND	—
East entry, floor	—	—	0.315
Basement recreation room, floor	ND	—	—
Basement recreation room, south floor	ND	—	—
South bedroom, floor	ND	ND	—
Northwest bedroom, floor	ND	ND	0.251
Southwest bedroom, floor center	—	ND	—
Northeast bedroom, floor	—	—	ND
Dining room floor	—	—	0.256

Abbreviations: —, data not collected (a 100-cm² deposition pad could not be or was not placed in that location); ND, not detectable [results were less than the limit of detection (LOD = 0.067 µg/100 cm²); BLOQ, below limit of quantitation (LOQ = 0.20 µg/100 cm²). Values shown are in µg/100 cm².

^aDeposition pad placed directly under treated table.

^bDeposition pad appeared to have been stepped on.

Table 2. Summary of cumulative chlorpyrifos loading on deposition pads from houses treated with chlorpyrifos crack and crevice and spot applications

Time	House #1	House #2	House #3
-1 day	ND/ND	ND/ND	1.435/BLOQ
1 hr	ND/ND	ND/ND	0.397/0.225
2 hr	ND/ND	ND/ND	0.399/0.205
4 hr	ND/ND	ND/ND	0.378/0.211
8 hr	BLOQ/ND	BLOQ/ND	BLOQ/0.225
12 hr	BLOQ/BLOQ	ND/ND	0.623/0.233
1 day	BLOQ/BLOQ	ND/ND	2.298/0.271
2 days	BLOQ/BLOQ	BLOQ/ND	0.545/0.353
3 days	BLOQ/0.228	BLOQ/BLOQ	0.665/0.352
4 days	0.245/0.236	BLOQ/BLOQ	0.678/0.416
5 days	0.200/0.249	0.243/BLOQ	0.995/0.452
6 days	0.255/0.232	0.303/BLOQ	1.252/0.568
7 days	0.315/0.274	0.352/0.216	1.073/0.535
8 days	0.281/0.310	0.416/0.223	1.283/0.566
9 days	0.319/0.293	0.395/0.327	1.158/0.620
10 days	0.351/0.288	0.432/0.342	1.148/0.586

ND, not detected [results were less than limit of detection (LOD = 0.07 µg/100 cm²); BLOQ, below limit of quantitation (LOQ = 0.2 µg/100 cm²). Values shown are for family room/bedroom and are in µg/100 cm².

reported by the residents. Based on cumulative residues found on the deposition pads, the rate of nontarget deposition decreased over time, with negligible additional deposition and accumulation after approximately 7 days.

In addition to the 10-day cumulative deposition pads collected from two locations in the house, deposition pads were collected from all living area floors throughout the house at 2 hr after application to determine nontarget drift immediately after application. A summary of the 2-hr deposition pads can be found in Table 3. These results were generally in the range of the preexposure samples (Table 2), except for a single sample (9.9 µg/100 cm²), which was located directly beneath the treated kitchen table. Because of its proximity to a treated surface and the fact that it contained much more chlorpyrifos than the other 2-hr deposition samples, this sample was considered an outlier.

Dislodgeable residues (carpet drag and hard-toy wipes). Bioavailable, or dislodgeable, residues were negligible, as measured with the sled and the toy balls. In the bedroom of all three houses and the family rooms of houses #1 and #2, there were no detectable chlorpyrifos residues (LOD = 0.00005 µg/cm²) on carpet drag samples. Only the carpet drags from the family room of house #3 contained sufficient dislodgeable residues to detect, although all were below the method LOQ (0.00016 µg/cm²). Moreover, no detectable dislodgeable residues were measured (<LOD = 0.00065 µg/cm²) on the hard-toy dosimeters, with the exception of a single sample (one of 48

Table 4. Summary of urinary 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) levels (calculated chlorpyrifos amounts) from volunteers exposed to crack and crevice and spot applications of Dursban Pro

Volunteer (house, person)	Preexposure ($\mu\text{g/kg bw/day}$)	11-Day cumulative minus background ($\mu\text{g/kg bw}$) ^a	Average daily excretion (Absorbed chlorpyrifos) ($\mu\text{g/kg bw/day}$)
#1A	0.13 (0.31) ^b	0.40 (0.00–0.16/day)	0.037 ^c (0.090) ^d
#1B	0.07 (0.18)	0.34 (0.00–0.07/day)	0.031 (0.077)
#2A	0.04 (0.11)	0.39 (0.00–0.07/day)	0.036 (0.090)
#2B	0.09 (0.21)	0.01 (0.00–0.01/day)	0.001 (0.002)
#3A	0.31 (0.77)	0.11 (0.00–0.06/day)	0.010 (0.023)
#3B	0.35 (0.87)	0.03 (0.00–0.03/day)	0.003 (0.009)

^a11-Day cumulative 3,5,6-TCP = $\sum_{n=0 \text{ to } n=10} (\text{Urinary 3,5,6-TCP Concentration})_{\text{day } n} - (\text{Urinary Preapplication 3,5,6-TCP})_{\text{day } -1}$ ^bAbsorbed chlorpyrifos was calculated using the 3,5,6-TCP found on day-1 and the following formula:

$$\left(\begin{array}{c} \text{Background} \\ \text{exposure} \\ (\mu\text{g/kg bw/day}) \end{array} \right) = \left(\begin{array}{c} \text{3,5,6-TCP} \\ \text{Excreted on day -1} \\ (\mu\text{g/kg bw}) \end{array} \right) + \left(\begin{array}{c} 0.7151 \\ \text{(fraction of oral dose} \\ \text{eliminated in urine)} \end{array} \right) \times \left(\begin{array}{c} 350.6 \\ 198 \\ \text{(molecular weight} \\ \text{ratio of} \\ \text{chlorpyrifos to TCP)} \end{array} \right)$$

^cCalculated by dividing the 11-day cumulative 3,5,6-TCP ($\mu\text{g/kg bw/day}$) by 11.^dCalculated using the equation for preexposure chlorpyrifos and average daily 3,5,6-TCP excretion levels.**Table 5.** Estimated absorbed doses for children for each monitored house

Child	Estimated respiratory dose ($\mu\text{g/kg}$) ^a	Estimated dermal dose ($\mu\text{g/kg}$)	Estimated oral dose ($\mu\text{g/kg}$) ^b	Total estimated absorbed dose ($\mu\text{g/kg}$)	Margin of exposure (% of NOEL) ^c
House #1	0.19	ND ^d	0.07	0.26	385 (0.26)
House #2	0.62	ND	1.48	2.10	48 (2.10)
House #3	0.46	ND	0.34	0.80	125 (0.80)

Abbreviations: NOEL, no observed effect level; ND, not detected.

^aAssumed that 100% of inhaled chlorpyrifos was absorbed via pulmonary absorption; used the highest air concentration for calculation.^bUsed highest single residue result from deposition pads (Table 2) and assumed 100% of the residue was removed when mouthed.^cHuman NOEL of 100 $\mu\text{g/kg bw/day}$ corresponds to plasma cholinesterase inhibition. Margin of Exposure = (acute NOEL)/(Total Estimated Absorbed Dose).^dContributing residue values were zero, resulting in nondetectable dermal exposures.

hard-toy samples collected) from house #3 that contained 0.00199 $\mu\text{g/cm}^2$ chlorpyrifos at 8 hr after application in the family room, slightly above the analytical method LOQ of 0.00194 $\mu\text{g/cm}^2$ and probably the artifact of a chlorpyrifos-containing dust applied before the start of this study. Similarly, Lu and Fenske (14) recently reported that only 0.78% of chlorpyrifos applied directly to carpet was dislodgeable 1 hr after a broadcast application.

Previous studies have evaluated several dislodgeable residue techniques, including hand presses, weighted sleds, and surface rollers, for estimating the fraction of a surface residue that is dislodgeable (15). Hand press technique, (i.e., pressing bare hands on a treated surface and then washing the hands with solvent) generally dislodge less residue than sled and roller techniques due to the sheering motion of the sled (16). Therefore, the use of a sled technique should result in a conservative estimate of actual dislodgeable residues upon human contact with a surface (15).

Biomonitoring results. Chlorpyrifos doses actually absorbed by adult residents were assessed with biological monitoring techniques. By quantifying the amount of

chlorpyrifos metabolite excreted in the urine, the amount of chlorpyrifos absorbed via all routes can be calculated (10). In addition, biomonitoring of adults can be used to validate the route-specific exposure data as determined with the dosimetry techniques by comparing actual absorbed doses with exposures calculated from environmental measurements.

The volunteers were instructed to avoid exposure to chlorpyrifos during the week before application. Because the half-life for excretion of 3,5,6-TCP is approximately 24 hr (10), the volunteers would have reached a steady state of 3,5,6-TCP elimination on the day before application (day -1). Thus, the 3,5,6-TCP in their preexposure urine would represent their background exposure, as reported in Table 4. For all of the volunteers, the preapplication exposure urinary 3,5,6-TCP levels were consistent with reference concentration levels for the general population, at the 99th percentile, as reported by Hill et al. (17). By converting the 3,5,6-TCP excretion values into equivalent chlorpyrifos concentrations, the calculated preexposure chlorpyrifos exposure values ranged from 0.11 to 0.87 $\mu\text{g/kg body weight (bw)/day}$ for all study participants (Table 4).

The amount of 3,5,6-TCP in the urine was quantified for each of the 11 days of urine collection following application. Daily excreted 3,5,6-TCP levels for individual volunteers were low in comparison to their baseline exposures (Table 4). For all volunteers, the 11-day cumulative urinary 3,5,6-TCP amount excreted during the sampling period, with the individuals' background level subtracted, was calculated (Table 4). The excretion rate for 3,5,6-TCP over time is well understood (10). However, because the volunteers were potentially reexposed to chlorpyrifos each time they reentered their home, use of an excretion rate from a one-time exposure was not appropriate. Therefore, the daily average amount of 3,5,6-TCP excreted during the entire sampling period was calculated (Table 4). The daily average 3,5,6-TCP amount was subsequently used to calculate the daily average amount of chlorpyrifos absorbed.

Discussion

Potential absorbed chlorpyrifos doses may be estimated for residents within the treated homes. Total multipathway exposures may consist of respiratory, dermal, and oral exposures. Although biological monitoring was performed exclusively for the adults, exposures to children may be estimated using the residue measurements collected with passive dosimetry.

Child's respiratory exposure. Potential exposures may be estimated for residents within the treated homes. Respiratory exposures to children were estimated using the following exposure equation:

$$\text{Child's Respiratory Dose } (\mu\text{g/kg bw/day}) = C \times D \times BR/bw \quad (1),$$

where C = highest measured air concentration at the 0.4-m height ($\mu\text{g/m}^3$ /day); D = estimated time spent within treated home [0.831 days (child) (18)]; BR = individual respiratory rate [6.5 m^3/day (child) (19)]; and bw = body weight [child bw = 20 kg (4)].

Maximum air concentrations measured in each structure were used to calculate conservative potential daily respiratory doses for children living in each home. As a result, estimated inhalation doses were 0.19, 0.62, and 0.46 $\mu\text{g/kg bw/day}$ based on air concentrations of 0.7 $\mu\text{g/m}^3$, 2.3 $\mu\text{g/m}^3$, and 1.7 $\mu\text{g/m}^3$ (Figure 1 A–C) for houses #1, #2, and #3, respectively (Table 5). All daily 24-hr time-weighted average (TWA) air concentrations measured at 0.4 m were less than 1.6 $\mu\text{g/m}^3$ (Table 1), which is at least fivefold lower than the NAS guideline of 10 $\mu\text{g/m}^3$ (20). In addition, the highest 12-hr TWA air concentration was 2.3 $\mu\text{g/m}^3$ (Fig. 1B, 60–72 hr).

Therefore, even the highest instantaneous exposure is approximately four times less than the NAS guideline.

Child's nondietary oral and dermal doses. Potential nondietary oral doses from licking a soft toy located in a treated or high activity room can be estimated by using the following general exposure equation:

$$\text{Nondietary oral dose} = \frac{TR \times DR_T \times SA_T}{bw} \quad (2),$$

where TR = total residue on the deposition pad surface ($\mu\text{g}/100 \text{ cm}^2/\text{day}$), representative of a soft toy (Tables 2, 3); DR_T = dislodgeable residue from toy due to chewing (= 100%); SA_T = surface area of soft toy [300 cm^2 (4)]; and bw = body weight [child $bw = 20 \text{ kg}$ (4)].

Estimated nondietary oral doses were 0.07, 1.48, and $0.34 \mu\text{g}/\text{kg bw}/\text{day}$ based on maximum residues of 0.44, 9.9, and $2.3 \mu\text{g}/100 \text{ cm}^2$ measured on deposition pads in houses #1, #2, and #3, respectively (Table 5). As mentioned earlier (see deposition pads results), although the dosimetry sample containing $9.9 \mu\text{g}/100 \text{ cm}^2$ seemed to be an outlier from this data set given the negligible residues found on all the other pads, this sample was still included in this analysis. A child's exposure is largely a function of the amount of residue present on a toy surface and the amount of residue that may be dislodged upon licking or mouthing it. The quantity of chlorpyrifos removed from a surface by an aqueous (polar) solvent such as saliva was not estimated in this work. Instead, the calculations used the conservative assumption that all of the chlorpyrifos residue found on the deposition pad could be removed by a child's saliva. As a result, mouthing frequency was not important to this evaluation. The oral-exposure calculation provided a conservative estimate of nondietary exposure because the assumption was made that the child chewed on the soft toy containing the highest cumulative residues on a deposition pad and that all of the surface residue was subsequently ingested (Tables 2, 3).

Accumulation of semivolatile pesticides on surfaces within the home following broadcast application have recently been reported by Gurunathan et al. (4). In that study, cumulative residues on foam-containing felt toys ($10,000\text{--}80,000 \mu\text{g}/100 \text{ cm}^2$) located in treated apartment rooms were at least four orders of magnitude greater than the amount measured on the deposition pads following crack and crevice application. The residue differences may be explained by the differences in the type of application, the volume of pesticide applied, and the nature of the dosimeters used. In addition,

Gurunathan et al. (4) did not evaluate the amount of residue transferred from the toy. Extraction of a matrix with a nonpolar organic solvent, as conducted by Gurunathan et al. (4), probably would remove more chlorpyrifos residue than expected following either casual human contact with the surface of a toy or placement of an object in one's mouth, as evidenced by dislodgeable residue results. The need to use a nonpolar solvent versus an aqueous solvent to efficiently desorb residues from denim dosimeters likely supports this assumption (21).

Potential dermal exposure to children can be assessed by using the following general exposure equation:

Dermal exposures from contact with household surfaces in high activity rooms =

$$DR_C \times SA_C \times DA/bw \quad (3),$$

where DR_C = dislodgeable residue from carpet ($\mu\text{g}/\text{m}^2$), SA_C = surface area contacted by crawling child [$0.1\text{--}2.2 \text{ m}^2/\text{day}$ (13)], DA = dermal absorption [1% (10)], and bw = body weight [child $bw = 20 \text{ kg}$ (4)].

Because only a single carpet dislodgeable residue and hard-toy wipe sample contained any detectable residues (the single sample contained only $0.006 \mu\text{g}/\text{m}^2$ above the LOQ and may be due to an earlier application), the likelihood of chlorpyrifos residues being transferred from a surface to a child is remote. Moreover, if minimal nontarget residues deposited onto household surfaces are contacted by the resident, less than 3% of the chlorpyrifos will be absorbed through the skin (10). Houghton et al. (16) reported actual transfer coefficients from chlorpyrifos-containing upholstery to human hands of approximately 0.05–0.71% following an indoor application. If the deposited chlorpyrifos is physically adsorbed onto or into the matrix, chlorpyrifos residues may not be available upon contact. Therefore, because this route would contribute little to a child's overall potential exposure, dermal exposures were excluded from this exposure assessment (Table 5).

Risk assessment for children. The total estimated absorbed dose for a child from all potential routes following a crack and crevice application are summarized in Table 5. Since air measurements indicated that chlorpyrifos dissipates from the structure in 3–7 days and no further accumulation of surface deposition occurs within the same time period, comparison of exposures to an acute or short-term end point is appropriate for evaluating hazard (22). Thus, the toxicological end point used by the EPA following short-term oral exposure to chlorpyrifos, the

NOEL associated with plasma cholinesterase inhibition ($100 \mu\text{g}/\text{kg bw}/\text{day}$) was used for this study. The resulting margin of exposure [MOE; the ratio of the NOEL ($100 \mu\text{g}/\text{kg bw}/\text{day}$) to the absorbed dose] would be greater than 150. For this assessment, the conservative assumption was made that a child may be exposed to maximum air concentrations for 0.83 days (20 hr), although the highest concentrations lasted for only 12 hr or less. Since exposures associated with a crack and crevice (or spot) application are transient and decrease over a 7-day period after application and any actual absorbed dose of chlorpyrifos is rapidly metabolized and excreted (10), it is unlikely that there would be any cumulative effects from subsequent crack and crevice treatments separated by the minimum 7-day application interval on the product label.

Exposure assessment for adults. Biomonitoring results indicated that the daily average urinary 3,5,6-TCP excretion amounts, with background subtracted, were low and consistent with baseline measurements (Table 4). Although the urine of the volunteers #1B, #2A, and #3B showed an increase of 3,5,6-TCP on 0, 1, and/or 2 days consistent with the higher air concentrations, the biomonitored level on subsequent days was not consistent with expected patterns for chlorpyrifos exposure and subsequent 3,5,6-TCP excretion, based on reported pharmacokinetics (10). There was a slight increase of average 3,5,6-TCP excreted for each volunteer per day ($0.001\text{--}0.037 \mu\text{g}/\text{kg bw}/\text{day}$) (Table 4) following the application. This increase corresponds to $0.002\text{--}0.09 \mu\text{g}/\text{kg bw}/\text{day}$ of chlorpyrifos absorbed by each adult volunteer on average per day following the application. Therefore, the exposure from the crack and crevice treatment is approximately equal to or significantly less than background levels associated with typical dietary exposures from agricultural commodities. Chlorpyrifos equivalent levels, extrapolated from the 3,5,6-TCP measurements, are well below the NOEL of $100 \mu\text{g}/\text{kg bw}/\text{day}$ and result in an MOE of greater than 1,000.

Similarly, potential adult absorbed doses were calculated using the dosimetry data. Because potential dermal exposures to adults are expected to be negligible based upon the dislodgeable residue results, the air monitoring data may be sufficient to estimate total exposure to an adult. Respiratory exposures were calculated using the equations previously described for children, adjusting the values of the constants D , BR , and bw . Estimated inhalation exposures to adult women were calculated to be 0.096, 0.144, and $0.193 \mu\text{g}/\text{kg bw}/\text{day}$, based on maximum air

concentrations at the 1.3-m height of 0.8 $\mu\text{g}/\text{m}^3/\text{day}$, 1.1 $\mu\text{g}/\text{m}^3/\text{day}$, and 1.5 $\mu\text{g}/\text{m}^3/\text{day}$ (Fig. 1 A–C) for houses #1, #2, and #3, respectively (where $D = 0.67$ days (23), $BR = 11.3 \text{ m}^3/\text{day}$ (23), and $bw = 60 \text{ kg}$). Based on this evaluation, the resulting MOE is at least 500. Consequently, the absorbed doses, as precisely determined with biomonitoring, are considerably lower than estimates derived from the air monitoring measurements.

Conclusions

Air monitoring and dosimetry data were used to estimate chlorpyrifos exposure to adults and children following a crack and crevice application. By employing a monitoring scheme that evaluated potential surface and air residues in both treated rooms and adjacent untreated rooms of high activity, potential multipathway exposures were evaluated. Inhalation exposure was determined to be the dominant exposure pathway for the adult residents. For adults, the calculated MOE was approximately 500 and greater than 1,000, based upon the dosimetry and biomonitoring results, respectively.

In addition, children's estimated absorbed doses were calculated from the air monitoring and dosimetry data. The dosimetry data suggested low respiratory, oral, and dermal exposures for children playing in treated or adjacent rooms, even when conservative assumptions were used. The results presented in this paper suggest that redeposited chlorpyrifos residues were not generally bioavailable. In most cases, no detectable residues were dislodged by the carpet drags or the hard-toy wipes, and, therefore, were presumably not bioavailable for humans contacting these surfaces. The conservatively estimated total absorbed dose for children ranged from 0.26 to 2.1 $\mu\text{g}/\text{kg bw}/\text{day}$, or 0.26–2.1% of the

acute NOEL for plasma cholinesterase inhibition (Table 5). The comprehensive multipathway exposure evaluation for residents following crack and crevice treatments supports the safety of this use pattern. High margins of exposure calculated for children and adults indicate that neither subpopulation would receive an exposure of biological significance following a crack and crevice application.

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